

# Maleation of Linear Low-Density Polyethylene by Reactive Processing

NORMAN G. GAYLORD,\* RAJENDRA MEHTA, DORAISWAMY R. MOHAN, and VIJAY KUMAR

Gaylord Research Institute, New Providence, New Jersey 07974

## SYNOPSIS

The reaction of maleic anhydride (MAH) with molten 2 MI poly(ethylene-co-butene-1) (LLDPE) at 160°C in the presence of peroxyesters ( $t_{1/2} < 10$  s) as catalysts resulted in the formation of a mixture of cross-linked and trichlorobenzene-soluble LLDPE-*g*-MAH. The soluble fraction constituted more than 50% of the mixture and had an MI of 0.0 and an MAH content ranging from 0.3 to 1.8 wt %. The presence of tri(nonylphenyl) phosphite (TNPP) in the LLDPE-MAH-*t*-butyl peroctoate (*t*BPO) reaction at 160°C increased the MI of the soluble product to 0.7–2. The amount of soluble polymer increased at higher TNPP concentrations while its MAH content ranged from 0.05 to 0.54 wt %, with most contents in the 0.2–0.3 wt % range. The color development that usually occurs in polyolefin-MAH reactions was reduced by the presence of TNPP. However, the reaction of TNPP with the peroxide and with the products from the thermal decomposition thereof reduced the availability of the excited species necessary for the appendage of MAH units onto the polyolefin.

## INTRODUCTION

The reaction of maleic anhydride (MAH) with molten polyolefins in the presence of a peroxide catalyst proceeds as a heterogeneous reaction due to the insolubility of molten MAH and results in the appendage of individual MAH units onto the polyolefin backbone, accompanied by cross-linking in the case of low-density polyethylene (LDPE)<sup>1</sup> and high-density polyethylene (HDPE)<sup>2</sup>, degradation in the case of polypropylene (PP),<sup>3</sup> and both cross-linking and degradation in the case of ethylene-propylene copolymer rubber (EPR).<sup>4</sup>

The cross-linking and/or degradation reactions result from the generation of radical sites on the polymer backbone, followed by coupling or disproportionation, respectively. Such sites, which arise from hydrogen abstraction, are generated in the presence of a peroxide due to the attack of radicals derived therefrom. When MAH is present, the

number of such sites, and, therefore, the extent of cross-linking and/or degradation, is increased.

The appendage of MAH to a polyolefin backbone occurs under the conditions that are necessary to promote MAH homopolymerization, i.e., using a peroxide catalyst at a temperature where it has a short half-life. Consequently, the cross-linking and/or degradation that accompanies the appendage of MAH units is considered to be due to radical generation on the polymer backbone by some intermediate in the homopolymerization of MAH. The presence of electron donors that inhibit the homopolymerization of MAH reduces or prevents these undesirable side reactions.<sup>5</sup>

Colored products are generated during the homopolymerization of MAH, i.e., in the presence of a free radical catalyst undergoing rapid decomposition, as well as during the graft copolymerization of MAH onto a molten polyolefin, under the same conditions. The interaction of MAH, a strong electron acceptor, and an electron donor compound results in the formation of colored complexes. When an electron donor is present during the peroxide-catalyzed reaction of MAH with a molten polyolefin, the resultant crude polymer has a lighter color than when the donor is absent. However, when the crude polymer is

\* To whom correspondence should be addressed at The Charles A. Dana Research Institute for Scientists Emeriti, Drew University, Madison, NJ 07940.

purified by precipitation from solution, the recovered MAH-containing polymer is considerably lighter or is free of color.

The present investigation was undertaken to study the peroxide-catalyzed maleation of linear low-density polyethylene (LLDPE), i.e., poly(ethylene-co-butene), which contains pendant ethyl groups. The reaction was conducted in the absence as well as in the presence of tri (nonylphenyl and dinonylphenyl)phosphite (TNPP) at 160°C. The relatively low reaction temperature and TNPP were used to minimize the usual color development in the PE-MAH-peroxide reaction product.

## EXPERIMENTAL

### LLDPE-MAH Grafting Reactions

The reaction was conducted under nitrogen with a 40.0 g charge of LLDPE (melt index 2 or 20) (Novacor Corp.) in a Brabender Plasticorder at 60 rpm, generally at 160°C. The polymer was permitted to flux in the chamber, which required about 2 min at 160°C. A mixture of MAH, catalyst, and TNPP, in the form of a paste, was added to the molten polymer in four equal portions at 2 min intervals. Nitrogen flow through the chamber was stopped during each addition step to prevent loss of MAH. After the last addition, mixing was continued for an additional 2 min. The total reaction time was 10 min, including flux time, and then the reaction mixture was removed from the chamber.

### Melt Index

The melt flow (g/10 min) of the LLDPE-*g*-MAH was determined in a Tinius-Olsen melt indexer at 190°C under a load of 2.160 kg (ASTM D1238, Condition E). The melt index of crude polymer at 190°C was found to be higher than that of polymer from which unreacted MAH had been removed. The latter was obtained by pressing a 5–10 mil film from the crude polymer at 340°F, using a press cycle of 5 min under 5,000 psig, followed by 2 min under 40,000 psig. The film was suspended in boiling water for 2 h to hydrolyze the unreacted MAH and remove it as water-soluble maleic acid. The film was wiped dry and then dried *in vacuo* overnight at 80°C, before the determination of the melt index.

### Soluble Polymer and Gel Content

The amount of soluble polymer was initially determined by heating a 5–6 g sample of crude polymer in 200 mL refluxing xylene at 130°C for 2–4 h. The

solution or suspension was then filtered through several layers of cheesecloth into 1000 mL acetone. The precipitated xylene-soluble polymer was filtered, dried *in vacuo* overnight at 40°C, and weighed to obtain the amount of soluble polymer. The cheesecloth containing the xylene-insoluble gel polymer was dried in an air oven at 75–80°C overnight and, after subtracting the weight of the cheesecloth, yielded the gel content of the polymer.

It was subsequently found that, in some cases, the high gel content, indicated by the amount of xylene-insoluble polymer collected on the cloth, was not consistent with the high melt index value. The failure of the xylene to dissolve high molecular weight, uncross-linked polymer, yielding high gel content values, was confirmed by using 250 mL 1,2,4-trichlorobenzene at 130–150°C. The amount of soluble polymer increased in some cases by as much as 30% when TCB was used as solvent in lieu of xylene.

To ensure the complete removal of TCB from the polymer precipitated by addition of the TCB solution to 1300 mL acetone, the precipitate was filtered and heated for 45 min at 60°C in 150–200 mL acetone to permit the latter to extract the TCB. The polymer was then filtered, dried *in vacuo* for 24 h at 80°C, and weighed in order to obtain the amount of soluble polymer.

### MAH Content of LLDPE-*g*-MAH

The MAH content of the soluble polymer or of the polymer purified by extraction with water was calculated from the acid value. The latter was obtained by heating about 0.5–0.7 g of polymer for 1 h in 200 mL of refluxing water-saturated xylene. The hot solution was titrated immediately with 0.05 *N* ethanolic KOH using 3–4 drops of thymol blue (1%) in DMF as the indicator. A 0.5–1 mL excess of KOH solution was added, and the deep blue color was back-titrated to a yellow endpoint by the addition of 0.05*N* isopropanolic HCl to the hot solution. The KOH solution was standardized against a solution of potassium hydrogen phthalate.

The acid number was converted to MAH content as follows:

$$\text{MAH (\%)} = \frac{\text{acid number (mg KOH/g)} \times 98}{2 \times 561}$$

## RESULTS AND DISCUSSION

### Grafting of MAH onto 20 MI LLDPE

A 20 MI LLDPE containing no antioxidant was examined to determine to what extent cross-linking occurred and reduced the MI of the LLDPE.

The LLDPE-MAH reaction was carried out at 160°C in the absence and in the presence of TNPP ("Polygard," Uniroyal), which was used as received, as were the peroxides used as catalysts. In these experiments, xylene was used to determine LLDPE-g-MAH solubility.

As shown in Table I, the polymer remained at least 89% xylene-soluble in the absence or presence of TNPP and/or MAH. The MI fell from 20 to less than 2 in the absence of TNPP, while it remained above 18 in the presence of TNPP. The MAH content of the xylene-soluble fraction was about 0.6 wt % in the absence of TNPP and fell to 0.2 wt % when TNPP was present. Apparently, because of the high MI of the initial LLDPE, indicative of the relatively low molecular weight, the chains undergo chain extension during the reaction with MAH in the presence of peroxide rather than cross-linking, to give a higher molecular weight polymer with a lower MI.

### Grafting of MAH onto 2 MI LLDPE

#### *In Presence of Benzoyl Peroxide*

The reaction of MAH with molten LLDPE (MI 2) was carried out at 160°C in the presence of 0.0625 wt % benzoyl peroxide (BP) ( $t_{1/2} = 4$  s) using LLDPE containing 0 and 100 ppm antioxidant. The reaction was conducted in the absence as well as in the presence of TNPP. Polymer solubility was determined in refluxing xylene.

As shown in Table II, in the absence of MAH and

TNPP, the presence of antioxidant in the LLDPE increased the amount of insoluble polymer. In the absence of TNPP and in the presence of MAH, the presence of antioxidant had no effect on the polymer solubility. In the presence of TNPP and MAH, the amount of insoluble polymer was not related to the presence of antioxidant. However, the latter decreased the MAH content of the xylene-insoluble polymer.

#### *In Presence of t-Butyl Peracetate*

*t*-Butyl peracetate (*t*BPA) ( $t_{1/2} = 80$  s at 160°C) was used as catalyst at a concentration of 0.0625 wt % based on LLDPE, in the reaction of MAH at 160°C with 2 MI LLDPE having no antioxidant.

Using the usual addition mode, wherein MAH-catalyst-TNPP was added to molten LLDPE in four shots, as shown in Table III, the presence of MAH decreased the amount of xylene-soluble polymer, while the presence of both MAH and TNPP increased the amount of xylene-soluble polymer while the MI decreased from 2.0 to 1.0. The presence of TNPP decreased the MAH content of the xylene-soluble polymer.

When the additives, i.e., MAH, *t*BPA, and TNPP were premixed with powdered LLDPE and the mixture was added to the heated chamber at 160°C over a 1 min period, in lieu of the usual 4-step addition of the additive mixture to the molten polymer over an 8 min period with a total mixing time of 10 min, the amount of xylene-soluble polymer was over 80%

**Table I LLDPE-MAH Reaction in Presence of Peroxyesters<sup>a</sup> (LLDPE MI 20)**

| Catalyst | MAH (g) | TNPP (g) | Addition Mode <sup>b</sup> | LLDPE-g-MAH                |                               |         |
|----------|---------|----------|----------------------------|----------------------------|-------------------------------|---------|
|          |         |          |                            | MI <sup>c</sup> (g/10 min) | Xylene-Soluble <sup>d</sup> % | MAH (%) |
| tBPO     | 0       | 0        | A                          | 17.1                       | 94                            | —       |
|          | 2       | 0        | A                          | 0.9                        | 89                            | 0.58    |
| tBPA     | 2       | 0.37     | A                          | 18.0                       | 92                            | 0.24    |
|          | 2       | 0        | A                          | 1.8                        | 92                            | 0.55    |
|          | 2       | 0.37     | A                          | 19.0                       | 92                            | 0.2     |
|          |         |          | B                          | 19.5                       | 90                            | 0.2     |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 20, AO 0 ppm), 0.025 g catalyst; total reaction time 10 min at 160°C.

<sup>b</sup> Addition mode: A = MAH-catalyst-TNPP paste added in four shots to molten LLDPE; B = PE-MAH-catalyst-TNPP mixture added in 1 min.

<sup>c</sup> Total crude polymer pressed into film and extracted with boiling water.

<sup>d</sup> Soluble in refluxing xylene at 130°C.

**Table II LLDPE-MAH Reaction in Presence of Benzoyl Peroxide<sup>a</sup> (LLDPE MI 2 with 0 or 100 ppm Antioxidant)**

| MAH<br>(g) | TNPP<br>(g) | AO in PE<br>(ppm) | LLDPE- <i>g</i> -MAH    |                                    |            |
|------------|-------------|-------------------|-------------------------|------------------------------------|------------|
|            |             |                   | Xylene Insoluble<br>(%) | Xylene-Soluble <sup>b</sup><br>(%) | MAH<br>(%) |
| 0          | 0           | 100               | 61                      | 39                                 | —          |
|            |             | 0                 | 34                      | 63                                 | —          |
| 1          | 0           | 100               | 67                      | 30                                 | 0.37       |
|            |             | 0                 | 67                      | 31                                 | 0.52       |
| 1          | 0.37        | 100               | 40                      | 55                                 | 0.09       |
|            |             | 0                 | 53                      | 35                                 | 0.14       |
| 2          | 0           | 100               | 65                      | 32                                 | 0.53       |
|            |             | 0                 | 65                      | 31                                 | 0.52       |
| 2          | 0.37        | 100               | 53                      | 42                                 | 0.27       |
|            |             | 0                 | 41                      | 55                                 | 0.43       |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2), 0.025 g catalyst; total reaction time 10 min at 160°C; addition mode MAH-BP-TNPP paste added in four shots to molten LLDPE.

<sup>b</sup> Soluble in refluxing xylene at 130°C.

(Table III). The amount of xylene-insoluble polymer decreased as the total mixing time was changed from 4 min to 10 min, while the MI of water-extracted film remained unchanged and the MAH content of 0.2–0.4 wt % showed little or no effect of mixing time.

When the additive package, i.e., premixed MAH, *t*BPA, and TNPP in the form of a paste was added in one shot to molten LLDPE, as would be the case

using an extruder with only one port for addition to the melt, with the low catalyst concentration employed, i.e., 0.0625 wt % based on LLDPE and 1.25 wt % based on MAH, the MAH content of the total polymer, after water extraction to remove unreacted MAH, was no higher than that obtained by the other procedures. However, the amount of xylene-soluble polymer and the MI were higher than obtained in the four-shot procedure (Table III).

**Table III LLDPE-MAH Reaction in Presence of *t*-Butyl Peracetate<sup>a</sup> (LLDPE MI 2)**

| MAH<br>(g) | TNPP<br>(g) | Addition<br>Mode <sup>b</sup> | Total Time<br>(min) | Crude Polymer                 |                         | LLDPE- <i>g</i> -MAH    |                                    |            |
|------------|-------------|-------------------------------|---------------------|-------------------------------|-------------------------|-------------------------|------------------------------------|------------|
|            |             |                               |                     | MI <sup>c</sup><br>(g/10 min) | MAH <sup>c</sup><br>(%) | Xylene Insoluble<br>(%) | Xylene-Soluble <sup>d</sup><br>(%) | MAH<br>(%) |
| 0          | 0           | A                             | 10                  |                               |                         | 27                      | 68                                 |            |
| 2          | 0           | A                             | 10                  |                               |                         | 67                      | 22                                 | 0.7        |
| 2          | 0.37        | A                             | 10                  | 1.0                           |                         | 39                      | 48                                 | 0.4        |
| 2          | 0.37        | B                             | 4                   | 2.0                           | 0.3                     | 23                      | 69                                 |            |
|            |             |                               | 6                   | 2.1                           | 0.2                     | 2                       | 91                                 |            |
|            |             |                               | 10                  | 2.3                           | 0.4                     | 5                       | 84                                 |            |
| 2          | 0.37        | C                             | 10                  | 1.8                           | 0.2                     | 27                      | 67                                 |            |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm), 0.025 g *t*BPA; reaction temperature 160°C.

<sup>b</sup> Addition mode: A = MAH-*t*BPA-TNPP paste added in 4 shots to molten LLDPE; B = PE-MAH-*t*BPA-TNPP mixture added in 1 min; C = MAH-*t*BPA-TNPP paste added in one shot to molten LLDPE.

<sup>c</sup> Total crude polymer pressed into film and extracted with boiling water.

<sup>d</sup> Soluble in refluxing xylene at 130°C.

**In Presence of *t*-Butyl Peroctoate**

*t*-Butyl peroctoate (*t*BPO),  $t_{1/2} = 6$  s at 160°C, was used as catalyst in the reaction of MAH with 2 MI LLDPE containing no antioxidant at 160°C, as well with 2 MI LLDPE containing 100 ppm antioxidant. The amount of xylene-soluble polymer was higher when antioxidant was present, independent of the amount of MAH charged and the absence or presence of TNPP (Table IV). This reflected the destruction of peroxide or radicals therefrom by the antioxidant and also resulted in lower MAH content in the xylene-soluble polymer. The amount of soluble polymer increased when TNPP was present but lower MAH contents were obtained. The higher the initial MAH charged, the higher the MAH content of the polymer.

Since the catalyst half-life is a function of temperature, the reaction of MAH with 2 MI LLDPE containing no antioxidant was carried out at 160, 175, and 190°C, using a higher MAH charge (10 wt % on LLDPE), a higher TNPP charge (2.5 wt % on LLDPE, 25 wt % on MAH), and higher *t*BPO charge (0.125–0.1875 wt % on LLDPE, 1.25–1.875 wt % on MAH) (Table V).

The MAH content of the water-extracted LLDPE-*g*-MAH increased and the MI decreased as the catalyst concentration increased. The MI decreased as the temperature increased, but there was little or no effect of temperature on the MAH content of the LLDPE-*g*-MAH. This may reflect that

there was no significant difference in catalyst half-life in the temperature range studied (Table V).

The concentrations of the various reactants were varied relative to the fixed 40.0 g charge of 2 MI LLDPE (0 ppm antioxidant) in the LLDPE-MAH reaction in the presence of TNPP at 160°C:

| Reactants     | g/40.0 g LLDPE | Wt % on LLDPE |
|---------------|----------------|---------------|
| <i>t</i> -BPO | 0.025–0.075    | 0.0625–0.1875 |
| MAH           | 0–4.0          | 0–10.0        |
| TNPP          | 0–1.0          | 0–2.5         |

The soluble polymer was determined by solution in 1,2,4-trichlorobenzene (TCB) at 130–150°C. The soluble polymer recovered by precipitation into acetone and extraction with acetone was analyzed for MAH content. The melt index was determined on water-extracted films pressed from total polymer.

The reactions conducted with different amounts of *t*BPO at 160°C are summarized in the following tables:

| Table | g/40.0 g LLDPE | % on LLDPE |
|-------|----------------|------------|
| VI    | 0.025          | 0.0625     |
| VII   | 0.050          | 0.1250     |
| VIII  | 0.075          | 0.1875     |

**Table IV LLDPE-MAH Reaction in Presence of *t*-Butyl Peroctoate<sup>a</sup> (LLDPE MI 2 with 0 or 100 ppm Antioxidant)**

| MAH (g) | TNPP (g) | AO in PE (ppm) | LLDPE- <i>g</i> -MAH |                                 |         |
|---------|----------|----------------|----------------------|---------------------------------|---------|
|         |          |                | Xylene Insoluble (%) | Xylene-Soluble <sup>b</sup> (%) | MAH (%) |
| 0       | 0        | 100            | 3                    | 88                              | —       |
|         |          | 0              | 34                   | 64                              | —       |
| 1       | 0        | 100            | 58                   | 41                              | 0.34    |
|         |          | 0              | 75                   | 22                              | 0.45    |
| 1       | 0.37     | 100            | 38                   | 58                              | 0.07    |
|         |          | 0              | 38                   | 55                              | 0.20    |
| 2       | 0        | 100            | 71                   | 24                              | 0.49    |
|         |          | 0              | 65                   | 29                              | 0.68    |
| 2       | 0.37     | 100            | 40                   | 55                              | 0.26    |
|         |          | 0              | 40                   | 50                              | 0.36    |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2), 0.025 g *t*BPO; total reaction time 10 min at 160°C; addition mode MAH-*t*BPO-TNPP paste added in four shots to molten LLDPE.

<sup>b</sup> Soluble in refluxing xylene at 130°C.

**Table V Effect of Reaction Temperature in LLDPE-MAH Reaction in Presence of *t*-Butyl Peroctoate<sup>a</sup> (LLDPE MI 2)**

| <i>t</i> BPO<br>(g) | Temp<br>(°C) | <i>t</i> BPO <i>t</i> <sub>1/2</sub><br>(s) | LLDPE- <i>g</i> -MAH          |                         |
|---------------------|--------------|---|-------------------------------|-------------------------|
|                     |              |   | MI <sup>b</sup><br>(g/10 min) | MAH <sup>b</sup><br>(%) |
| 0.05                | 160          | 6   | 1.93                          | 0.31                    |
|                     | 175          | 2   | 1.87                          | 0.25                    |
| 0.075               | 160          | 6   | 1.83                          | 0.42                    |
|                     | 175          | 2   | 1.80                          | 0.48                    |
|                     | 190          | 1   | 1.34                          | 0.41                    |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm), 4.0 g MAH, 1.0 g TNPP; total reaction time 10 min; addition mode MAH-*t*BPO-TNPP paste added in four shots to molten LLDPE.

<sup>b</sup> Total crude polymer pressed into film and extracted with boiling water.

Tables VI-VIII reveal that, independent of the concentration of reactants, the MAH content of the TCB-soluble LLDPE-*g*-MAH ranged from about 0.1 to 1.8 wt %, with most of the results in the 0.2-0.3 wt % range. The effect of the TNPP concentration was detectable in the amount of TCB-soluble uncross-linked polymer and in the MI, which also reflects the amount of uncross-linked polymer.

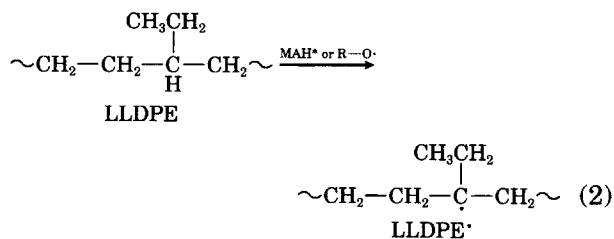
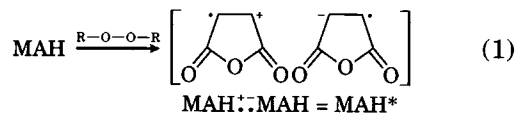
The effect of TNPP concentration was detectable in the amount of soluble, uncross-linked polymer and in the MI, which also reflects the amount of uncross-linked polymer.

The effect of *t*BPO concentration on the polymer solubility and MI, in the presence of MAH and the absence of TNPP, is shown in Table IX. It is apparent that, in general, the highest MAH contents were obtained as the catalyst concentration increased. The high solubility and the low MI as the catalyst concentration increased indicates that chain extension rather than cross-linking occurred under these conditions.

## MECHANISM

The mechanism of the reaction of MAH with molten polyolefins has been discussed earlier.<sup>2</sup> The reactive species is the excited monomer [MAH<sup>+</sup> · MAH] [eq. (1)], which also plays a role in the homopolymerization of MAH. The excimer is a hydrogen-abstracting species and therefore generates radical sites on the polymer [eq. (2)], which either undergoes cross-linking through coupling [eq. (3)] or degradation due to disproportionation or excimer addition

[eq. (4)]. The excimer may also add to the radical sites generated on the polymer under the influence of the species generated from peroxide decomposition:

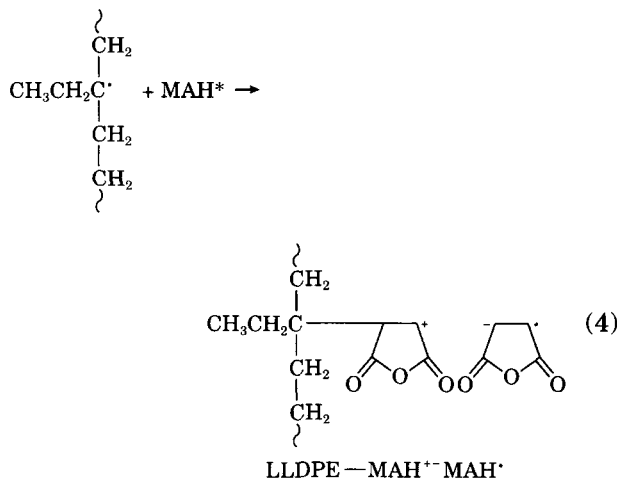
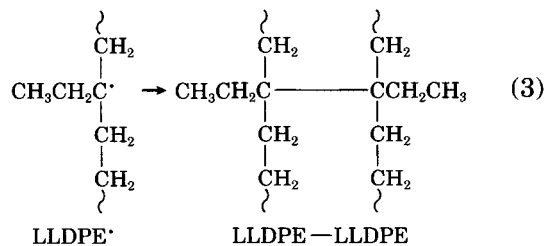
**Table VI Effect of Reactant Concentrations in LLDPE-MAH Reaction in Presence of *t*-Butyl Peroctoate<sup>a</sup> (0.0625% *t*BPO based on LLDPE)**

| MAH<br>(g) | TNPP<br>(g) | MI <sup>b</sup><br>(g/10 min) | LLDPE- <i>g</i> -MAH |                                 |
|------------|-------------|-------------------------------|----------------------|---------------------------------|
|            |             |                               | (%)                  | TCB-Soluble <sup>c</sup><br>(%) |
| 0          | 0           | 0.59                          | 92                   | —                               |
| 1.0        | 0           | 0.00                          | 78                   | 0.62                            |
|            | 0.37        | 1.47                          | 73                   | 0.19                            |
|            | 0.5         | 1.09                          | 60                   | 0.17                            |
|            | 0.75        | 1.36                          | 57                   | 0.20                            |
|            | 1.0         | 0.70                          | 89                   | 0.37                            |
| 2.0        | 0           | 0.00                          | 59                   | 0.86                            |
|            | 0.37        | 1.93                          | 50                   | 0.17                            |
|            | 0.5         | 1.82                          | 76                   | 0.15                            |
|            | 0.75        | 2.04                          | 58                   | 0.24                            |
|            | 1.0         | 2.13                          | 84                   | 0.54                            |
| 3.0        | 0           | 0.00                          | 52                   | 0.58                            |
|            | 0.37        | 1.27                          | 78                   | 0.07                            |
|            | 0.5         | 2.07                          | 98                   | 0.28                            |
|            | 0.75        | 1.35                          | 86                   | 0.34                            |
|            | 1.0         | 1.58                          | 91                   | 0.27                            |
| 4.0        | 0           | 0.00                          | 79                   | 1.64                            |
|            | 0.37        | 1.99                          | 90                   | 0.27                            |
|            | 0.5         | 2.21                          | 85                   | 0.25                            |
|            | 0.75        | 2.30                          | 91                   | 0.42                            |
|            | 1.0         | 2.34                          | 93                   | 0.34                            |

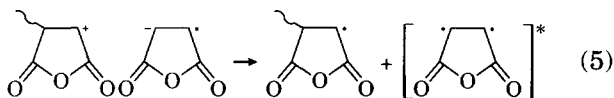
<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm), 0.025 g *t*BPO, total reaction time 10 min at 160°C; addition mode MAH-*t*BPO-TNPP added in four shots to molten LLDPE.

<sup>b</sup> Total crude polymer pressed into film and extracted with boiling water.

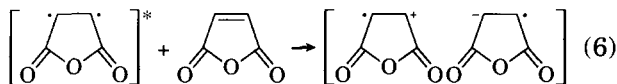
<sup>c</sup> Soluble in trichlorobenzene at 130-150°C.



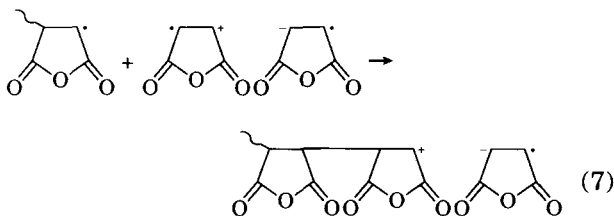
The pendant  $\text{MAH}^+$  cation takes an electron from the counterion, i.e., the  $\text{MAH} \cdot$  anion radical and generates an  $\text{MAH}^+$  radical and an "activated" monomer [eq. (5)]:



The "activated" monomer donates an electron to  $\text{MAH}$  to form excimer [eq. (6)]:



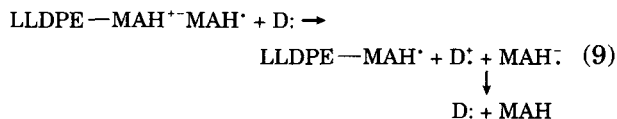
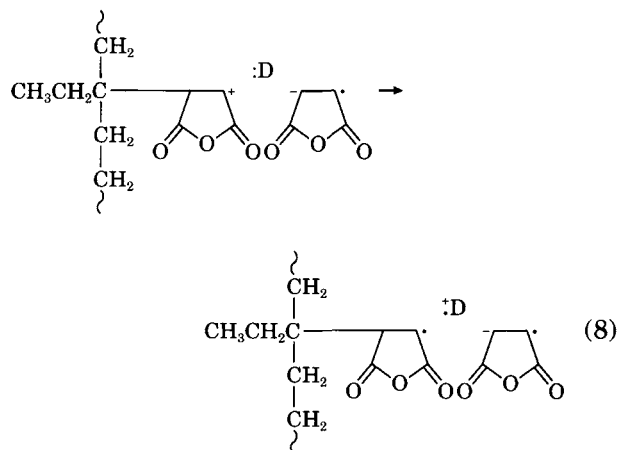
The  $\text{MAH}^+$  radical [eq. (5)] adds excimer to continue chain propagation, e.g., in  $\text{MAH}$  homopolymerization [eq. (7)]:



The presence of electron-donor compounds prevents  $\text{MAH}$  homopolymerization, presumably by

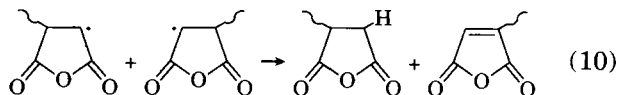
interfering with the propagation step. These compounds are effective in decreasing the extent of cross-linking while still permitting the appendage of  $\text{MAH}$  units, when they are present during the reaction of  $\text{MAH}$  with a polyolefin in the presence of a peroxide. The effective compounds presumably donate an electron to the cationic species resulting from excimer addition to the polymer radical.

Although  $\text{TNPP}$  is not an electron donor per se, phosphites undergo oxidation by reaction with peroxides and the resultant phosphate is presumably the effective electron donor:



Because of the conversion of the  $\text{MAH}^+$  cation to an  $\text{MAH} \cdot$  radical, the generation of "activated" monomer and excimer, as shown in eqs. (5) and (6), are prevented and cross-linking is minimized. The  $\text{MAH}$ -containing polymer formed in the presence of the electron donor contains individual  $\text{MAH}$  units, the same as when formed in the absence of the donor.

When the polymerization of  $\text{MAH}$  is conducted at elevated temperatures, low yields of very low molecular weight polymer or no polymer are obtained. This is due to the tendency for the radical at the end of the chain [eq. (5)] to participate in termination by disproportionation or for the cation at the end of the chain [eq. (7)] to participate in a proton-transfer reaction, as shown in eqs. (10) and (11), respectively:



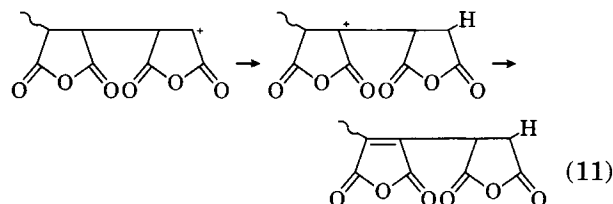
**Table VII Effect of Reactant Concentrations in LLDPE-MAH Reaction in Presence of *t*-Butyl Peroctoate<sup>a</sup> (0.125% *t*BPO based on LLDPE)**

| MAH<br>(g) | TNPP<br>(g) | LLDPE- <i>g</i> -MAH          |                                 |            |
|------------|-------------|-------------------------------|---------------------------------|------------|
|            |             | MI <sup>b</sup><br>(g/10 min) | TCB-Soluble <sup>c</sup><br>(%) | MAH<br>(%) |
| 0          | 0           | 0.03                          | 94                              | —          |
| 1.0        | 0           | 0.00                          | 96                              | 1.52       |
|            | 0.37        | 0.52                          | 82                              | 0.15       |
|            | 0.5         | 0.93                          | 73                              | 0.30       |
|            | 0.75        | 1.23                          | 72                              | 0.31       |
|            | 1.0         | 1.75                          | 42                              | 0.10       |
| 2.0        | 0           | 0.00                          | 46                              | 1.32       |
|            | 0.37        | 0.86                          | 64                              | 0.17       |
|            | 0.5         | 1.21                          | 51                              | 0.13       |
|            | 0.75        | 1.52                          | 85                              | 0.26       |
|            | 1.0         | 1.48                          | 86                              | 0.22       |
| 3.0        | 0           | 0.00                          | 50                              | 1.15       |
|            | 0.37        | 1.11                          | 51                              | 0.19       |
|            | 0.5         | 1.22                          | 87                              | 0.37       |
|            | 0.75        | 2.21                          | 77                              | 0.29       |
|            | 1.0         | 2.19                          | 65                              | 0.05       |
| 4.0        | 0           | 0.00                          | 29                              | 0.72       |
|            | 0.37        | 2.11                          | 61                              | 0.28       |
|            | 0.5         | 1.87                          | 71                              | 0.24       |
|            | 0.75        | 2.11                          | 93                              | 0.17       |
|            | 1.0         | 1.80                          | 91                              | 0.31       |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm), 0.050 g *t*BPO, total reaction time 10 min at 160°C; addition mode MAH-*t*BPO-TNPP added in four shots to molten LLDPE.

<sup>b</sup> Total crude polymer pressed into film and extracted with boiling water.

<sup>c</sup> Soluble in trichlorobenzene at 130–150°C.



When the polymerization of MAH is conducted in the presence of a polymer at elevated temperatures, i.e., the attempted grafting of MAH onto a molten polymer in the presence of a peroxidic catalyst, no homopolymer of MAH is recovered and the appended MAH is present as individual units rather than as chains with multiple MAH units or oligomers. Although it has been proposed<sup>7,8</sup> that the appendage of individual MAH or succinic anhydride units to the molten polymer results from conducting

the reaction at temperatures above 150°C, which is considered to be the ceiling temperature for MAH polymerization, it is proposed herein that the hydrogen-transfer reactions in eqs. (10) and (11), and particularly the latter that involves cationic species, are responsible for the appendage of single anhydride units. Cationic reactions, including polymerization, are preferably conducted at low temperatures due to the occurrence of transfer reactions at higher temperatures and the limitation imposed thereby on molecular weight of the resultant polymer.

The participation of cationic intermediates in the homopolymerization of MAH cannot be discounted. Poly-MAH is a brittle, colored solid, having a high molecular weight by light-scattering measurements and a low molecular weight by viscosity measurements. This is indicative of a highly branched structure, consistent with proton-transfer reactions on

**Table VIII Effect of Reactant Concentrations in LLDPE-MAH Reaction in Presence of *t*-Butyl Peroctoate<sup>a</sup> (0.1875% *t*BPO based on LLDPE)**

| MAH<br>(g) | TNPP<br>(g) | LLDPE- <i>g</i> -MAH          |                                 |            |
|------------|-------------|-------------------------------|---------------------------------|------------|
|            |             | MI <sup>b</sup><br>(g/10 min) | TCB-Soluble <sup>c</sup><br>(%) | MAH<br>(%) |
| 0          | 0           | 0.00                          | 89                              | —          |
| 1.0        | 0           | 0.00                          | 72                              | 1.17       |
|            | 0.37        | 0.42                          | 51                              | 0.25       |
|            | 0.5         | 0.77                          | 68                              | 0.26       |
|            | 0.75        | 0.81                          | 75                              | 0.30       |
|            | 1.0         | 1.60                          | 47                              | 0.30       |
| 2.0        | 0           | 0.00                          | 60                              | 1.79       |
|            | 0.37        | 0.86                          | 52                              | 0.19       |
|            | 0.5         | 1.40                          | 83                              | 0.25       |
|            | 0.75        | 1.08                          | 89                              | 0.24       |
|            | 1.0         | 1.20                          | 75                              | 0.34       |
| 3.0        | 0           | 0.00                          | 61                              | 1.40       |
|            | 0.37        | 1.11                          | 90                              | 0.31       |
|            | 0.5         | 0.96                          | 60                              | 0.33       |
|            | 0.75        | 1.22                          | 77                              | 0.28       |
|            | 1.0         | 1.75                          | 69                              | 0.20       |
| 4.0        | 0           | 0.00                          | 66                              | 0.56       |
|            | 0.37        | 0.84                          | 71                              | 0.24       |
|            | 0.5         | 0.86                          | 54                              | 0.23       |
|            | 0.75        | 0.80                          | 45                              | 0.21       |
|            | 1.0         | 1.30                          | 87                              | 0.33       |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm), 0.075 g *t*BPO, total reaction time 10 min at 160°C; addition mode MAH-*t*BPO-TNPP added in four shots to molten LLDPE.

<sup>b</sup> Total crude polymer pressed into film and extracted with boiling water.

<sup>c</sup> Soluble in trichlorobenzene at 130–150°C.



**Table IX LLDPE-*g*-MAH Preparation with *t*-Butyl Peroctoate in Absence of TNPP<sup>a</sup> (LLDPE MI 2, AO 0 ppm)**

| <i>t</i> BPO<br>(g) | MAH<br>(g) | LLDPE- <i>g</i> -MAH          |                          |            |
|---------------------|------------|-------------------------------|--------------------------|------------|
|                     |            | MI <sup>b</sup><br>(g/10 min) | TCB-Soluble <sup>c</sup> |            |
|                     |            |                               | (%)                      | MAH<br>(%) |
| 0.025               | 0          | 0.59                          | 92                       | —          |
|                     | 1.0        | 0.0                           | 78                       | 0.62       |
|                     | 2.0        | 0.0                           | 59                       | 0.86       |
|                     | 3.0        | 0.0                           | 52                       | 0.58       |
|                     | 4.0        | 2.3                           | 93                       | 0.34       |
| 0.050               | 0          | 0.0                           | 94                       | —          |
|                     | 1.0        | 0.0                           | 95                       | 1.52       |
|                     | 2.0        | 0.0                           | 46                       | 1.32       |
|                     | 3.0        | 0.0                           | 50                       | 1.15       |
|                     | 4.0        | 0.0                           | 29                       | 0.72       |
| 0.075               | 0          | 0.0                           | 89                       | —          |
|                     | 1.0        | 0.0                           | 72                       | 1.17       |
|                     | 2.0        | 0.0                           | 60                       | 1.79       |
|                     | 3.0        | 0.0                           | 61                       | 1.40       |
|                     | 4.0        | 0.0                           | 66                       | 0.56       |

<sup>a</sup> Reactants 40.0 g LLDPE (MI 2, AO 0 ppm); MAH-*t*BPO added in four shots to molten LLDPE; reaction time 10 min at 160°C.

<sup>b</sup> Total crude polymer pressed into film and extracted with boiling water.

<sup>c</sup> Soluble in trichlorobenzene at 130–150°C.

polymer, presumably by excimers or propagating chains. The same considerations would be valid for MAH polymerization in the presence of a molten polyolefin.

The formation of colored products from the reactions of MAH with molten polymers provides support for cationic intermediates, which could yield products with conjugated unsaturation.

## REFERENCES

1. N. G. Gaylord and M. Mehta, *J. Polym. Sci. Polym. Lett. Ed.*, **20**, 481 (1982).
2. N. G. Gaylord, R. Mehta, V. Kumar, and M. Tazi, *J. Appl. Polym. Sci.*, **38**, 359 (1989).
3. N. G. Gaylord and M. K. Mishra, *J. Polym. Sci. Polym. Lett. Ed.*, **21**, 23 (1983).
4. N. G. Gaylord, M. Mehta, and R. Mehta, *J. Appl. Polym. Sci.*, **33**, 2549 (1987).
5. N. G. Gaylord and R. Mehta, *J. Polym. Sci. Polym. Chem. Ed.*, **26**, 1189 (1988).
6. N. G. Gaylord, *Appl. Polym. Symp.*, **26**, 197 (1975).
7. K. E. Russell and E. C. Kelusky, *J. Polym. Sci. Part A Polym. Chem.*, **26**, 2273 (1988).
8. N. C. Liu, W. E. Baker, and K. E. Russell, *J. Appl. Polym. Sci.*, **41**, 2285 (1990).

Received May 17, 1991

Accepted June 10, 1991